The effect of volatile residues in burnt household items on the detection of fire accelerants

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Common household items were partially burnt and then sampled for volatile pyrolytic products using passive headspace adsorption. The adsorbed volatiles were then thermally desorbed and analyzed with capillary column gas chromatography. On comparing the results with those for corresponding unburnt samples, it was found that only a small proportion of the volatiles detected in the burnt items were pyrolytic products, the rest of the volatiles were attributed to residues originally present in the unburnt items. Even though volatile residues could be the sources of interference, they would not be mistaken for commonly used fire accelerants due to the absence of peak profiles that are characteristic of gasoline, kerosene or diesel. Although the presence of toluene as a pyrolytic product in some of the burnt samples might be mistaken for the use of paint thinner, the use of control samples prevents such misinterpretation. Similar experiments using one-month old items in place of newly prepared items showed that interference to the identification of commonly used fire accelerants became less likely as the volatile residues evaporated.

Des objets de ménage habituels ont été partiellement brûlés, puis les produits volatiles de pyrolyse ont été obtenus en utilisant une adsorbtion passive par espace de tête. Les produits volatiles adsorbés ont ensuite été désorbés thermiquement et analysés par chromatographie en phase gazeuse capillaire. En comparant les résultats avec ceux d'échantillons correspondants non brûlés, il a été possible de déterminer qu'une petite proportion des produits volatiles détectés dans les échantillons brûlés étaient des produits de pyrolyse. Le reste des volatiles a été attribué à des résidus présents à l'origine dans le matériel non brûlé. Bien que les résidus volatiles aient pu être source des interférences, ils ne pouvaient pas être confondus avec des produits accélérateurs de feu habituels, à cause de l'absence de profils de pics qui sont caractéristiques de l'essence, du kérosène, ou du diesel. Bien que la présence de toluène puisse être confondue avec l'utilisation de diluants pour peinture comme produit de pyrolyse dans certains des échantillons brûlés, l'utilisation, d'échantillons de contrôle prévient de telles interprétations fausses. Des expériences similaires, en utilisant des matériaux âgés d'un mois à la place des échantillons préparés récemment, ont montré que l'interférence pour l'identification des produits accélerateur de feu utilisés communément était de moins en moins probable, puisque les résidus volatiles s'étaient évaporés.

Mittels passiver Headspace Adsorption wurden die flüchtigen Pyrolyseprodukte von gewöhnlichen, teilweise verbrannten Haushaltsgegenstände gesammelt. Die adsorbierten Pyrolyseprodukte wurden anschließend thermisch desorbiert und mit Hilfe der Kapillar-Gaschromatochraphie analysiert. Der Vergleich dieser Ergebnisse mit jenen, die an entsprechenden jedoch unverbrannten Proben gewonnen wurden, zeigt, dass es sich nur bei einem geringen Anteil der flüchtigen Stoffe um Pyrolyseprodukte aus den verbrannten Proben handelte. Der Rest der flüchtigen Stoffe konnte Rückständen zugeordnet werden, die ursprünglich auch in den unverbrannten Gegenständen vorlagen. Obwohl flüchtige Rückstände Störungen in Chromatogrammen verursachen können, dürfen diese nicht mit gebräuchlichen Brandbeschleunigern verwechselt werden, da ihnen die characteristischen Peakprofile von Benzin, Kerosin oder Diesel fehlen. Obgleich die Anwesenheit von Toluol als Pyrolyseprodukt in einigen der verbrannten Proben mit dem Einsatz von Fabverdünner als Brandbeschleuniger verwechselt werden könnte, verhindert der Einsatz von Kontrollproben solche Fehlinterpretationen. Vergleichbare Experimente mit einem Monat alten Gegenständen anstelle frisch präparierter zeigen, dass derartige Schwierigkeiten bei der Identifizierung gebräuchlicher Brandbeschleuniger durch das Abdampfen der flüchtigen Rückstände reduziert werden können.

Se quemaron parcialmente diversos items domésticos y se muestrearon para análisis de productos volátiles de pirólisis usando adsorción pasiva de espacio de cabeza. Los volátiles adsorbidos fueron después desorbidos y analizados por cromatografía de gases con columna capilar. Cuando se compararon los resultados con los correspondientes items sin quemar se encontró que solo una pequeña parte de los volátiles detectados en los items quemados eran productos de pirólisis, el resto de los volátiles fueron atribuidos a residuos presentes originalmente en los items sin quemar. Aun cuando los residuos volátiles puedan ser fuentes de interferencia no pueden ser confundidos por acelerantes de fuegos de uso común debido a la ausencia de perfiles de picos que son característicos de gasolina, keroseno o diesel. Aunque la presencia de tolueno como producto de pirólisis en alguna de las muestras quemadas puede confundirse con un thinner de pinturas, el uso de muestras control previene dicha confusión. Experimentos similares utilizando items de un mes atrás en lugar de recientemente preparados demostraron que la interferencia para la identificación de los aceleradores comunes era menor a medida que los residuos volátiles se evaporaban.

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Key words Forensic science, fire accelerant analysis, fire debris analysis, pyrolytic products, volatile residues.

Introduction

The examination of fire debris samples for fire accelerant residues, supplemented by fire scene investigation, provides extremely useful evidence in proving the incendiary element of arson. Although a number of methods have been designed for this purpose [1–6] the task of distinguishing any significant signals from potential background interference coming from pyrolytic products remains one of the most daunting problems. It has been recognized that the interpretation of chromatographic profiles could be greatly complicated by the presence of pyrolytic products resulting from the combustion of synthetic materials [7,8]. For instance, pyrolysed materials may generate volatiles that are chemically similar to the components of targeted fire accelerants [9]. Depending on the type of polymer, thermal decomposition could result in the formation of compounds such as toluene, xylene and other complex volatiles [10]. This problem becomes particularly significant in situations where flammable residues are in fact absent or are present only in trace amounts. Obviously, the pyrolytic volatiles generated may lead to misinterpretation of data if not a false-positive response [11,12]. Thus, even if a great effort is made to facilitate the interpretation of chromatographic profiles [13,14], an accelerant can still go undetected or be incorrectly classified.

The purpose of this paper is to investigate whether or not partial burning of frequently encountered household items would produce pyrolytic products that could be confused with commonly used fire accelerants such as paint thinner, gasoline, kerosene and diesel. In Hong Kong, 'paint thinner' refers to an organic solvent available in the domestic market that contains mainly toluene with traces of minor components such as acetone, ethyl acetate and xylenes. Such a solvent is equivalent to 'lacquer thinner' in the West.

Experimental method

Sample preparation and volatiles recovery

A number of common household items (Table 1) including printed materials, structural materials for interior design, floorings, adhesives and finishes were obtained from local suppliers. These were put together in the way they are normally used or applied. Note that the carpets and doormat were newly purchased with unknown manufacturing date.

Table 1 List of item/item-pairs investigated in this study.

Newspaper	Printout (HP LaserJet 4 laser printer)
Magazine	Photocopy (Toshiba 4010 photocopier)
Carpets + Sponge rubber padding	Doormat
Oak floorboard + Asphalt	Plastic flooring + PVC adhesive
Veneer plywood + Contact adhesive	Pine wood + White glue
Wallpaper + Wallpaper paste	Beech wood + Lacquer
Cherry wood + Paint spray	Shoe + Shoe polish
Plaster + Emulsion paint	

In addition to samples of newly prepared items, one-month old samples were also needed for comparison. Hence, two sets of samples were prepared for each item/item-pair. The 'old' samples were unsealed and kept at ambient temperature for one month before they were further analyzed.

The volatile residues present in the burnt and unburnt items were recovered using passive headspace adsorption with Tenax TA (mesh size 60/80) as the adsorbent (Supelco Inc., Supelco Park, Bellefonte, PA 18823-0048, USA,or through Perkin-Elmer Corp., 761 Main Avenue, Norwalk, CT 06859, USA). The samples and the adsorbent tubes were kept together in sealed nylon bags for two days at room temperature or three hours at 80°C.

Burning of items was carried out with a Bunsen flame inside a fume cupboard until about half of the sample was consumed. The ignited samples were extinguished with a water sprayer and then kept in sealed nylon bags.

Instrumental analysis

The analysis was carried out using either an Automated Thermal Desorber-Gas Chromatography-Flame Ionization Detector (ATD-GC-FID) or an ATD-GC-MS (Mass Spectrometry) system. All instruments and controlling software were from the Perkin-Elmer Corporation. First, an ATD-50 or an ATD-400 was used in the recovery of volatiles from the Tenax TA tubes, after which the components of the volatiles were separated by a Restek RTX-5 nonpolar capillary column (5% diphenyl- 95% dimethyl polysiloxane, 0.25 mm i.d. × 30 m, 0.25 μm thick bonded phase) housed in an AutoSystem GC (Table 2). Lastly, the signals were detected with an FID or an MS (Q-Mass 910

Table 2 GC operating parameters of ATD-GC-FID and ATD-GC-MS systems.

	ATD-GC-FID	ATD-GC-MS
Carrier gas	Nitrogen	Helium
ATD-GC transfer line	130°C	200°C
Oven temperature	90°C for 2 min	75°C for 2 min
	90°C to 175°C in 8 min	75°C to 175°C in 10 min
	175°C for 5 min	175°C for 5 min
	175°C to 220°C in 9 min	175°C to 200°C in 5 min
	220°C for 6 min	200°C for 5 min
Detector temperature (FID)	300°C	N/A
Auxiliary Zone (MS)	N/A	180°C

Table 3 Identities of the volatiles in new samples before and after burning.

Sample	Volatiles detected before burning	Volatiles detected after burning
Newspaper	Diesel	Diesel
Magazine	Diesel-like	Non-significant
Printout from laser printer	Toluene	Non-significant
Printout from photocopier	Non-significant	Non-significant
Carpet (polypropylene)	Carbon disulphide	Carbon disulphide
+ Sponge rubber padding		Benzene
		Toluene
		Styrene
		Limonene
Carpet (nylon)	Carbon disulphide	Toluene
+ Sponge rubber padding		
Carpet (wool)	Carbon disulphide	Toluene
+ Sponge rubber padding		
Doormat	Carbon disulphide	Carbon disulphide
	Ethyl acetate	
	Benzene	Benzene
	Toluene	Toluene
		Styrene
Plastic flooring + PVC adhesive	Acetone	
	Cyclohexanone	Cyclohexanone
Oak floorboard + Asphalt	Toluene	Non-significant
Pine + White glue	Cyclohexanone	
	α-Pinene	α-Pinene
	β-Pinene	β-Pinene
Veneer plywood + Contact adhesive	Ethyl acetate	Ethyl acetate
	Benzene	Benzene
	Heptane	Heptane
	Toluene	Toluene
	Ethylbenzene	Ethylbenzene
	m-Xylene	m-Xylene
Wallpaper + Wallpaper paste	Non-significant	Non-significant
Plaster + Emulsion paint	Toluene	Toluene
White beech + Lacquer	2-Methyl-1-propanol	2-Methyl-1-propanol
	1-Butanol	1-Butanol
	Toluene	Toluene
	Butyl acetate	Butyl acetate
	Ethylbenzene	Ethylbenzene
	m-Xylene	m-Xylene
	p-Xylene	
Cherry wood + Paint spray	2-Methyl-1-propanol	2-Methyl-1-propanol
	2-Methylpropyl acetate	2-Methylpropyl acetate
	Butyl acetate	Butyl acetate
Shoe + Shoe polish	Mineral turpentine	Mineral turpentine

Benchtop quadrupole mass spectrometer). The data were collected by a Digital DECstation LPV+ 466d2 Personal Computer through proprietary interface cards using the Turbochrom Chromatography Workstation for FID signal and Q-Mass 910 Analytical Workstation for MS signal.

Data interpretation

Data interpretation was first attempted on an ATD-GC-FID chromatogram of the sample by comparing it to a collection of chromatograms of fire accelerant standards (Figure 1). When the technique of pattern recognition was not applicable to the FID chromatograms, ATD-GC-MS chromatograms were taken. Individual components in the MS chromatograms were then determined from searching in the NIST/EPA/MSDC library and their identities were reported when the matching scores were satisfactory.

Results and discussion

The use of both new and old samples in the experiment is to investigate the extent of dissipation of residual volatiles in air

Figure 1 ATD-GC-FID chromatograms of fire accelerant standards.

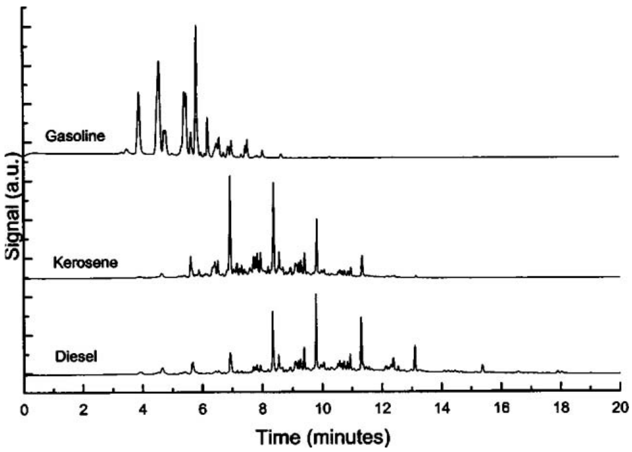


Figure 2 ATD-GC-FID chromatograms of new newspaper before and after burning.

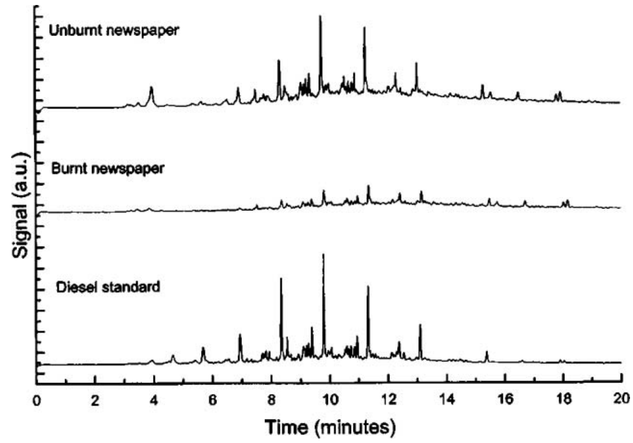


Figure 3 ATD-GC-MS chromatograms of polypropylene carpet and padding (a) before burning, (b) after burning.

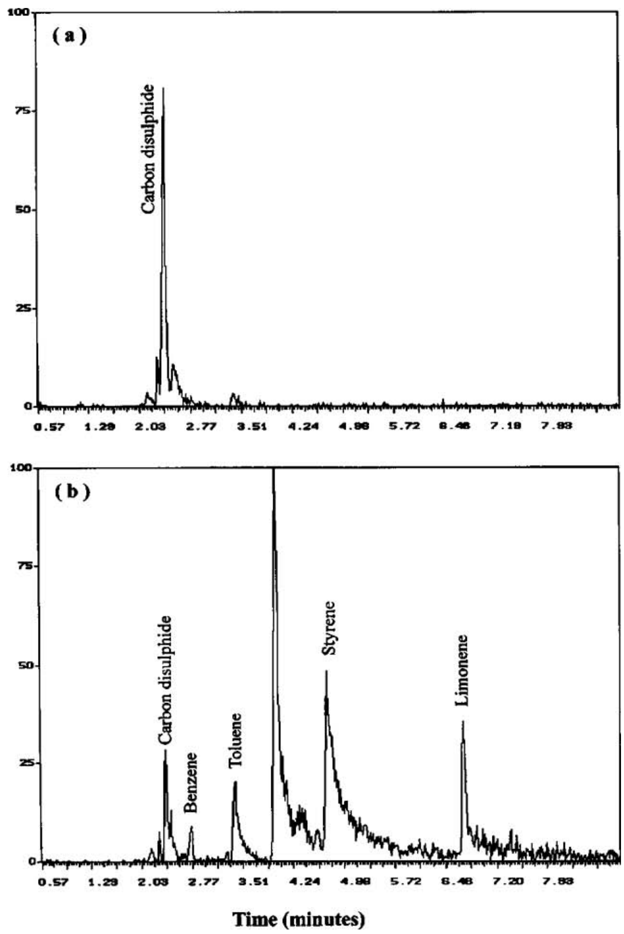


Figure 4 ATD-GC-MS chromatograms of doormat (a) before burning, (b) after burning.

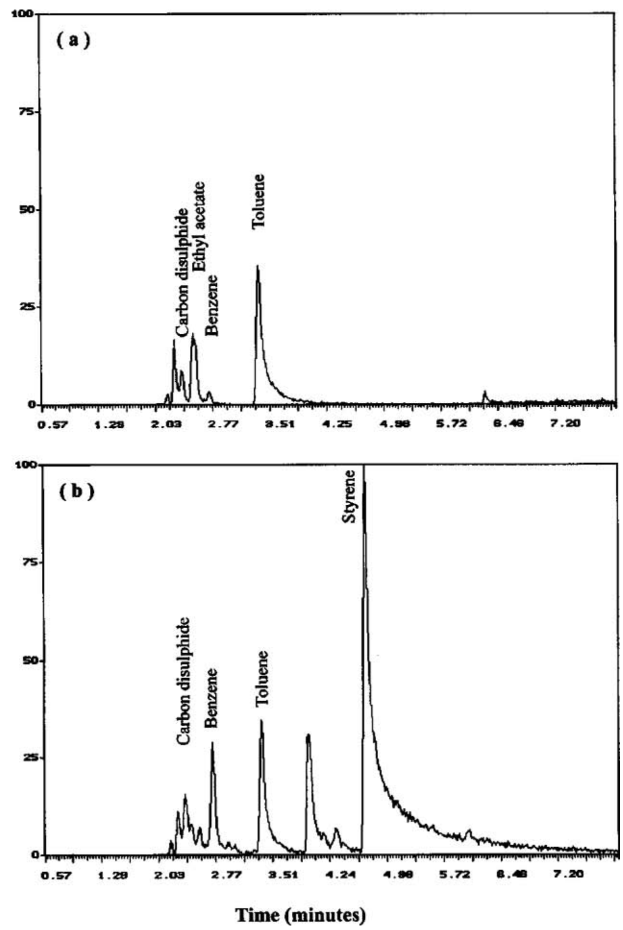


Table 4 Identities of the volatiles in old samples before and after burning.

Sample	Volatiles detected before burning	Volatiles detected after burning
Newspaper	Non-significant	Non-significant
Magazine	Non-significant	Non-significant
Printout from laser printer	Toluene	Non-significant
Printout from photocopier	Non-significant	Non-significant
Plastic flooring + PVC adhesive	Cyclohexanone	Cyclohexanone
Oak floorboard + Asphalt	Toluene	Non-significant
Pine + White Glue	α-Pinene β-Pinene	α-Pinene β-Pinene
Veneer plywood + Contact adhesive	Ethyl acetate Benzene Heptane Toluene	Ethyl acetate Benzene Heptane Toluene
Wallpaper + Wallpaper paste	Non-significant	Non-significant
Plaster + Emulsion paint	Toluene	Toluene
White beech + Lacquer	2-Methyl-1-propanol 1-Butanol Toluene Ethylbenzene	2-Methyl-1-propanol 1-Butanol Toluene
Cherry wood + Paint spray	2-Methyl-1-propanol 2-Methyl-propyl acetate Butyl acetate	2-Methyl-1-propanol 2-Methyl-propyl acetate Butyl acetate
Shoe + Shoe polish	Non-significant	Non-significant

after one month. To facilitate a semi-quantitative comparison, the same Tenax tube and the same sampling condition were used before and after the specimens were burnt.

Tables 3 and 4 summarize the results of the volatile products recovered from the new and old samples, before as well as after they were burnt. The chromatograms are in Figures 2–13. Use of the same vertical scales in the chromatograms for the unburnt and burnt samples in the figures facilitates visual comparison of the change in the amount of volatile residues before and after each item was burnt.

In Table 1 the items investigated are divided into four main groups, namely: printed materials, floorings, adhesives and finishes. Printed materials are relevant in the sense that newspapers and magazines are commonly found at home while printouts from printers or photocopiers are ubiquitous in offices. With all of the printed materials tested, none produced any pyrolytic products. However, the presence of a diesel-like pattern in the sample of burnt new newspaper should not be dismissed by the analyst (Figure 2). This is because in situations where there is no control sample (i.e., when unburnt newspaper of the same kind is unavailable), the presence of a diesel-like pattern would mistakenly suggest the use of fire accelerant. Nevertheless, the absence of any signal in the old newspaper sample shows that one month is long enough for all volatiles to be dissipated from newspapers. Therefore, if available, the date of print of burnt newspaper should be noted and precautions should be taken with those that are less than a month old.

Carpets, doormat, plastic and oak floorboards fall into the category of floorings. In Hong Kong, wooden floorboards are widely used inside apartments and doormats are commonly found at the entrances of premises. Traces of carbon disulphide were detected in three different kinds of unburnt carpets (made of polypropylene, nylon and wool respectively). This originated from the rubber padding materials underneath the carpets. Upon burning, all three burnt carpets gave off toluene, the major constituent of paint thinner (i.e. lacquer thinner). However, the amount of toluene detected was in such a trace level that it does not indicate the presence of fire accelerant in the sample. Unlike the other two types of carpets, burning of the polypropylene carpet also produced a number of other pyrolytic products such as limonene and benzene (Figure 3). Although limonene is a flammable terpene, unlike turpentine it is not commonly available in the local market and has not been used by arsonists. Similarly, despite benzene being a constituent of gasoline, it is not a commonly used fire accelerant by itself. Therefore, the presence of traces of benzene and limonene in burnt polypropylene carpet would not lead to a false-positive

Figure 5 ATD-GC-MS chromatograms of new veneer plywood and contact adhesive (a) before burning, (b) after burning.

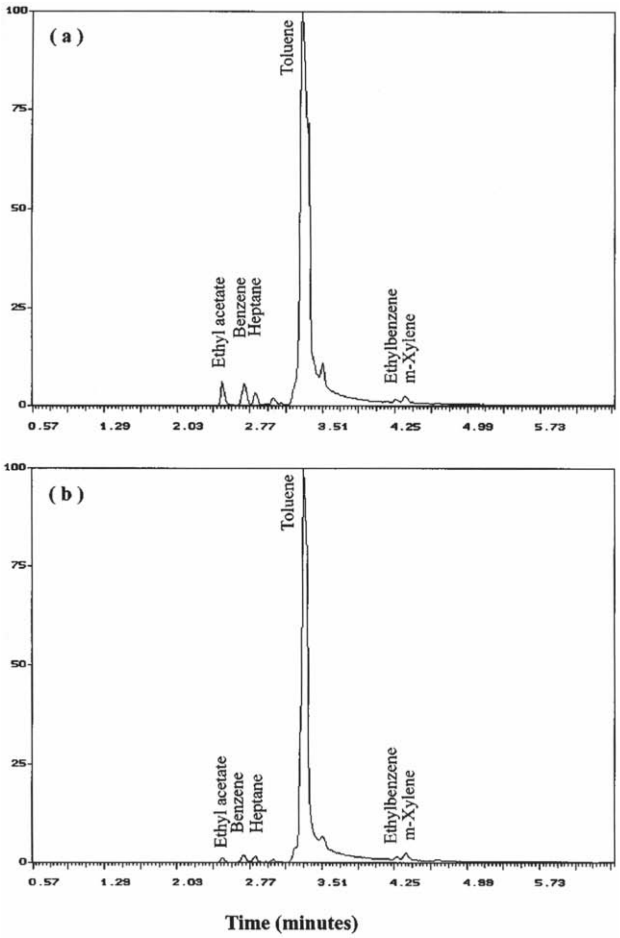
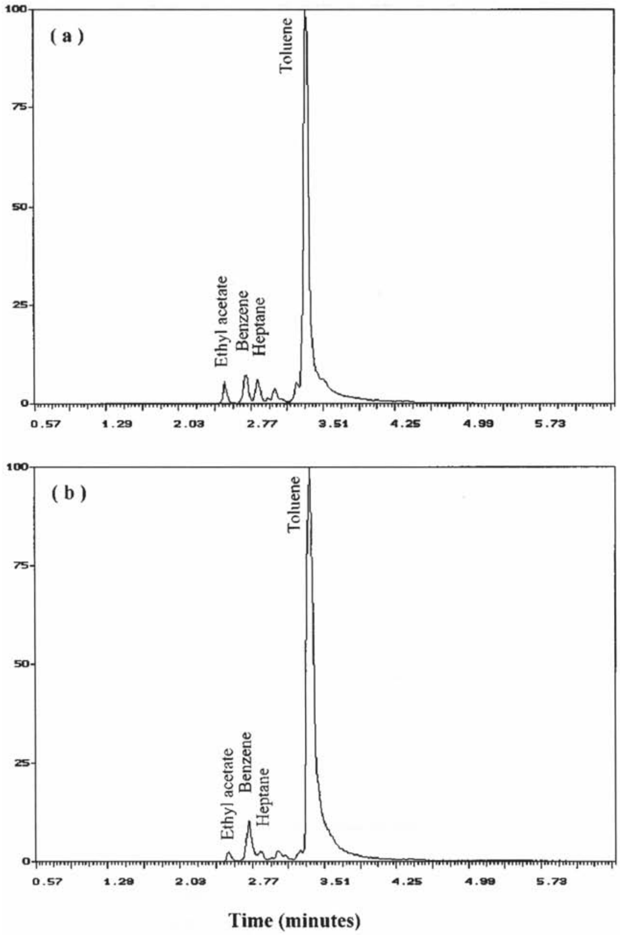


Figure 6 ATD-GC-MS chromatograms of old veneer plywood and contact adhesive (a) before burning, (b) after burning.



conclusion. Apart from substances showing a resemblance to fire accelerants, other volatiles like styrene were also detected. Since styrene is a common pyrolytic product of polystyrene, this suggests the presence of polystyrene in the polypropylene carpet.

In addition to carbon disulphide, ethyl acetate and toluene were recovered from the unburnt doormat (Figure 4a). These probably came from the glue applied to fix the top layer onto the bottom layer of the doormat. When the doormat (composed of nylon and styrene-butadiene copolymer) was burnt, styrene was again produced as one of the pyrolytic products (Figure 4b). But with regard to the likely possibility of being constituents of common fire accelerants, benzene, toluene and ethylbenzene are the significant ones. This is because some locally formulated solvents in the local market consist of mainly toluene with traces of benzene and ethylbenzene.

Of the four adhesives tested (white glue, PVC adhesive, contact adhesive and wallpaper paste), only contact adhesive was found to contain fire accelerant components. These include benzene, heptane, toluene, ethylbenzene and m-xylene. As shown in Figure 5, these six components were present both before and after a new sample was burnt. However, the results from the one-month old sample shown in Figure 6 indicate that only three components (benzene, heptane and toluene) persisted. This suggests that the old sample contained far fewer volatiles than the new sample and therefore it is less likely to cause interference in fire debris analysis.

Apart from new newspaper and contact adhesive, items newly finished with lacquer, paint spray and shoe polish were also found to contain volatile residues of fire accelerant components or compounds that resemble fire accelerants. These volatile residues are common organic solvents present in the finishes. After burning, no extra volatile pyrolytic products were found and the amounts of volatile residues diminished from the amounts originally present in the unburnt samples (Figures 7–9). This can obviously be explained by evaporation and combustion. The analyst should exert extra care when lacquer or shoe polish is present in exhibits. This is because lacquer contains toluene and xylenes (Figure 7) and can be confused with some locally formulated solvent. Similarly, the C9–C11 paraffins in shoe polish (Figure 9) can be confused with mineral turpentine.

Figure 7 ATD-GC-MS chromatograms of new beech wood and lacquer (a) before burning, (b) after burning.

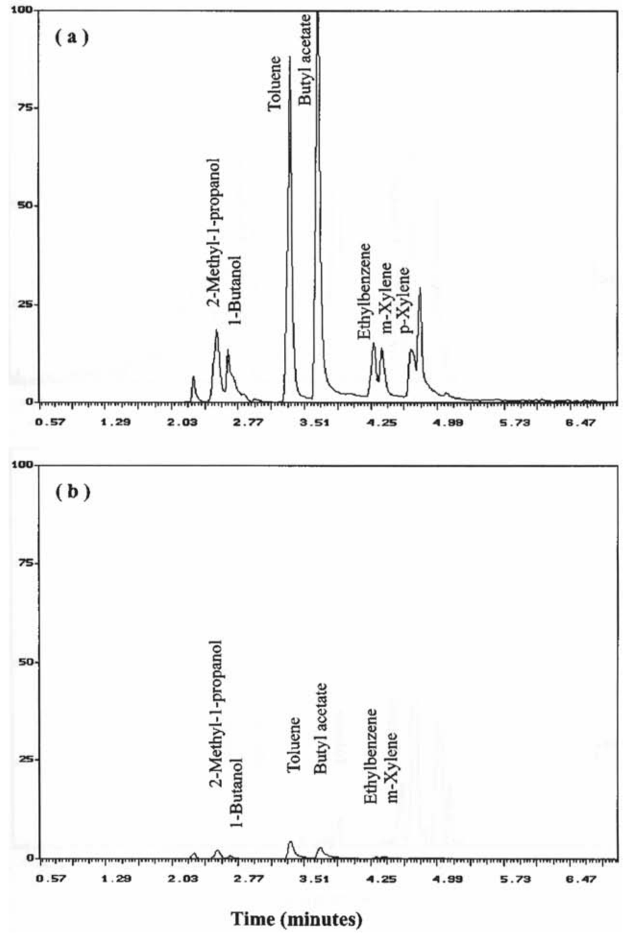
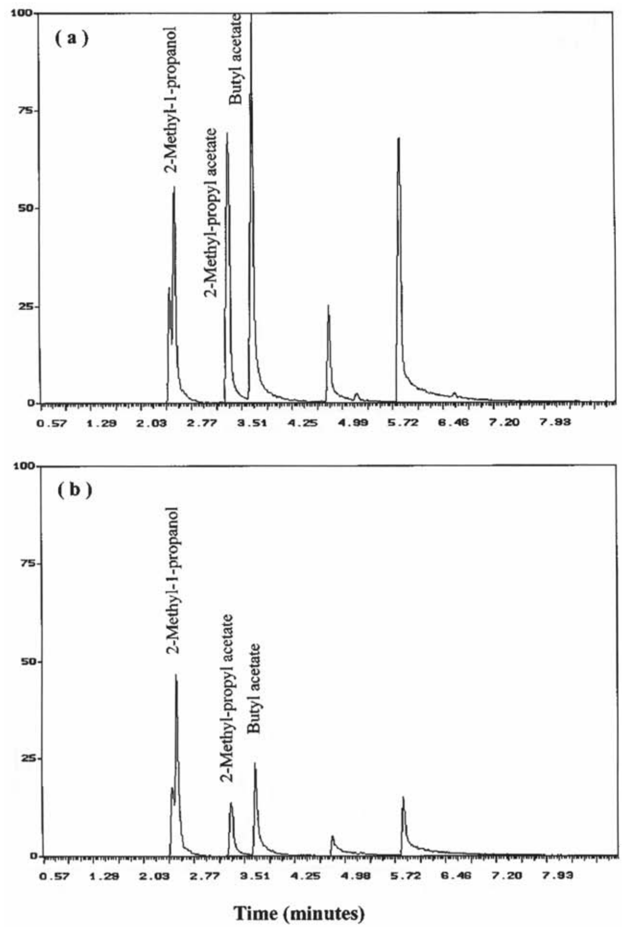


Figure 8 ATD-GC-MS chromatograms of new cherry wood and paint spray (a) before burning, (b) after burning.



Traces of volatile residues, particularly toluene, could also be found in unburnt plaster painted with emulsion paint (Figure 10a). The amount of toluene increased after the sample was burnt (Figure 10b). This could lead to an erroneous false-positive conclusion if an exhibit in the form of burnt emulsion paint on plaster is analyzed and then compared only to a control/comparison unburnt sample. One possible solution is to carry out the burning of an unburnt sample before comparison is made with the result of the exhibit.

The experimental results of the one-month old items finished with lacquer, paint spray and emulsion paint are shown in Figures 11–13. The results were similar to those of the newly prepared items except that the amount of volatile residues present in both the unburnt and burnt items had decreased. This once more confirms that interference to the identification of commonly used fire accelerants was less likely for one-month old items.

It is anticipated that further work on the dissipation rate of the volatiles from the newly prepared items through sampling at different time intervals would be useful. Moreover, the use of

Figure 9 ATD-GC-FID chromatograms of shoes with shoe polish before and after burning.

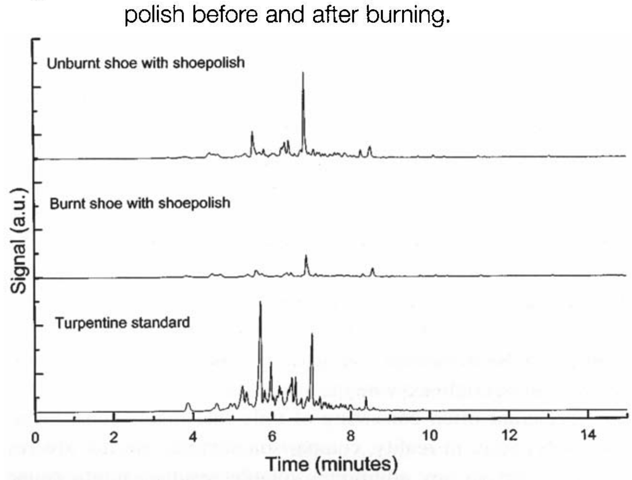


Figure 10 ATD-GC-MS chromatograms of new plaster and emulsion paint (a) before burning, (b) after burning.

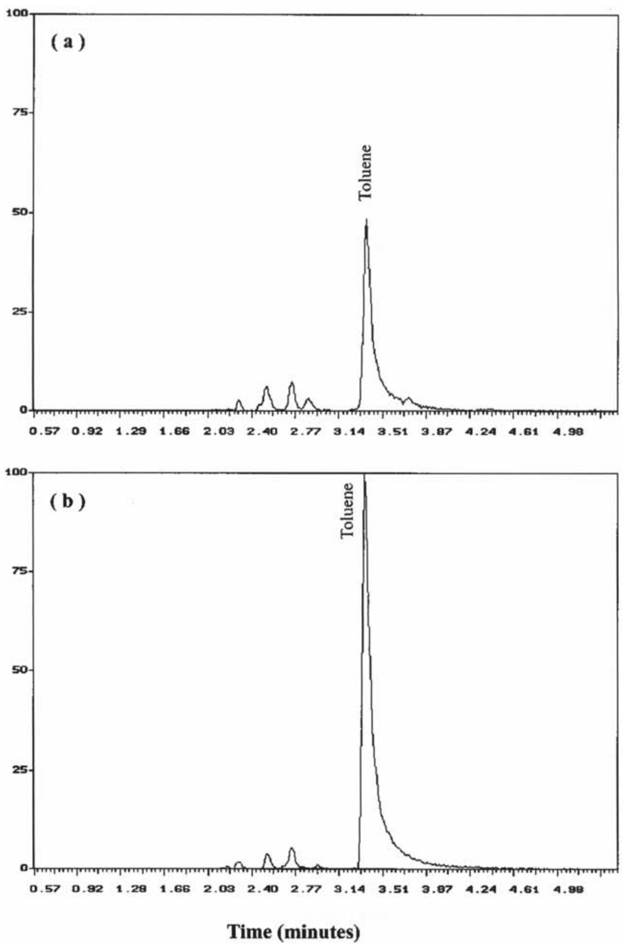
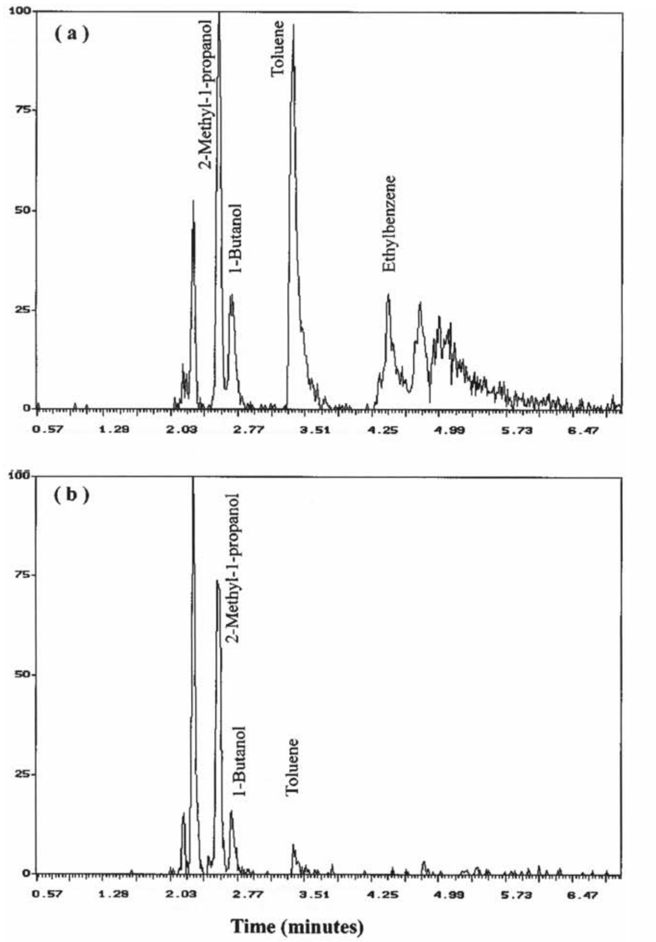


Figure 11 ATD-GC-MS chromatograms of old beech wood and lacquer (a) before burning, (b) after burning.



other common adsorbents such as activated charcoal in our experiments would suggest which adsorbent is least susceptible to interferences from the intrinsic and pyrolytic volatiles of common household items.

Conclusion

Passive headspace adsorption together with an automated desorption-gas chromatographic system particularly with a mass spectrometer as a detector provides a sensitive, effective and efficient way of sampling and separating volatiles in solid matrices. Although it is found from such a system that many newly prepared household items contain volatiles that could be sources of interference, the presence of control samples helps in distinguishing any signal from the background in the burnt samples. The volatiles that persist after the samples are burnt should not be dismissed, particularly when toluene is found, since it can be confused with the use of paint thinner – a common fire accelerant often consisting of only one major constituent. This is because, in reality, comparison samples are not always available and so any additional volatile residues might cause misinterpretation of other common fire accelerants. Furthermore, in comparing new and old burnt samples, it can be concluded that the latter contains fewer volatiles and pyrolytic products. Thus, old samples are less likely to be sources of interference compared to new samples. As a consequence, when there is an abundant choice of different objects at a fire scene for selection as exhibits for accelerant analysis, items that are clearly old rather than brand new are preferable. Otherwise, the fire investigators should at least note down and document any special conditions the exhibits were in. Lastly, the importance of fire scene investigation can hardly be over-emphasized since it provides information that is supplementary to that of laboratory analysis. It is not uncommon that only through a consideration of both fire scene investigation and laboratory analysis can the cause of a fire be found.

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Figure 12 ATD-GC-MS chromatograms of old cherry wood and paint spray (a) before burning, (b) after burning.

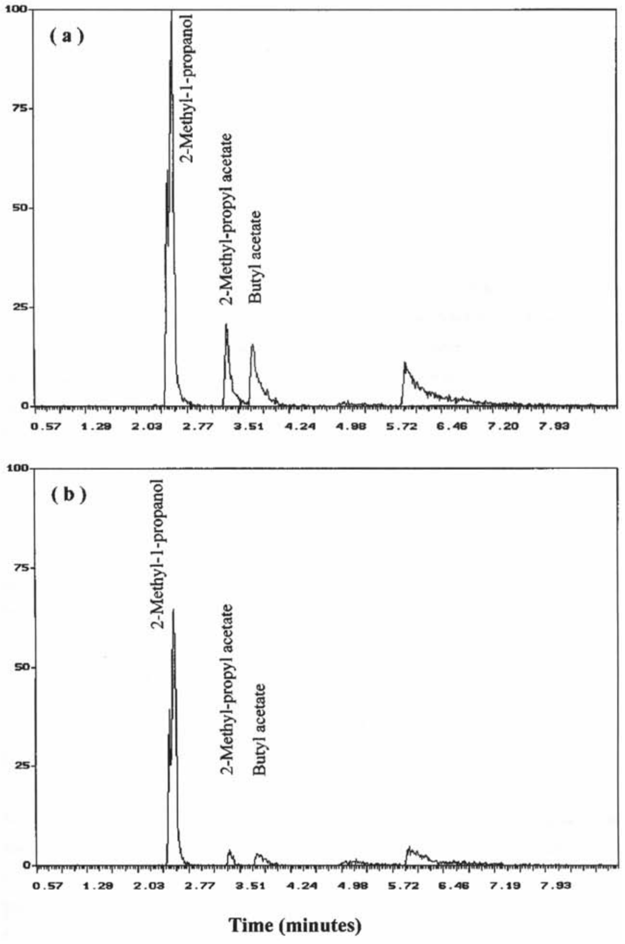
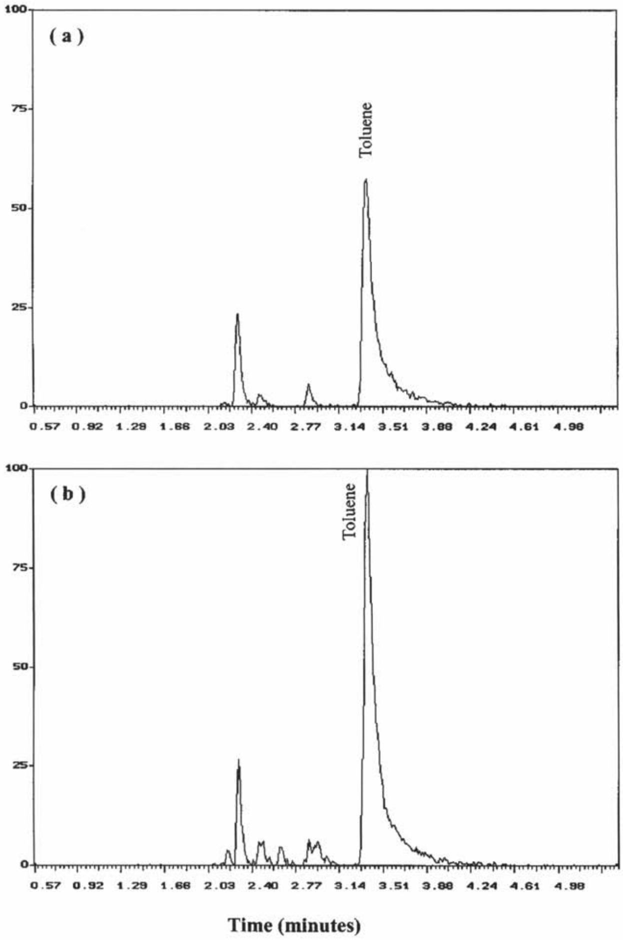


Figure 13 ATD-GC-MS chromatograms of old plaster and emulsion paint (a) before burning, (b) after burning.



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